

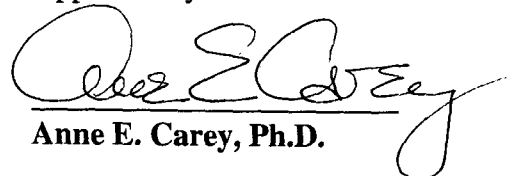
A Senior Thesis

**The Effect of Bedrock Geology on the Chemistry  
of Natural Waters in Central Ohio**

by  
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the requirements for the degree of  
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## INTRODUCTION

The principle streams and drainage areas of Central Ohio are contained within and affected by a variety of geologies and geomorphologies. This area provides an excellent medium in which to compare the effect of various sedimentary bedrock and surficial deposits on the chemistry of the natural waters.

Previous work on the relationships between geology and water chemistry has been done on the Amazon (Stallard and Edmond, 1983) and Mackenzie (Reeder et al, 1972) river systems. More recently, work with field and analytical methods including ion chromatography by Welch et al (1996) has significantly improved data accuracy while decreasing sources of error. These authors have shown that certain ions (Mg, Ca, Sr,  $\text{HCO}_3$ ,  $\text{SO}_4$ , K, B, Na, Cl, Si) are related to geology while others (F,  $\text{NO}_3$ , Ni, Cu, Zn) show more relationship to anthropogenic and other sources.

The objective of this project is to determine the major element chemistry of natural waters in two different bedrock systems using ion chromatography, colorimetric analysis, and wet chemistry. This project was run in conjunction with an urban effects project in the same study area coordinated by Dr. Anne E. Carey at The Ohio State University. The focus of this paper will be the comparative analysis of the geology and its effects on the geochemistry of natural waters of these two systems.

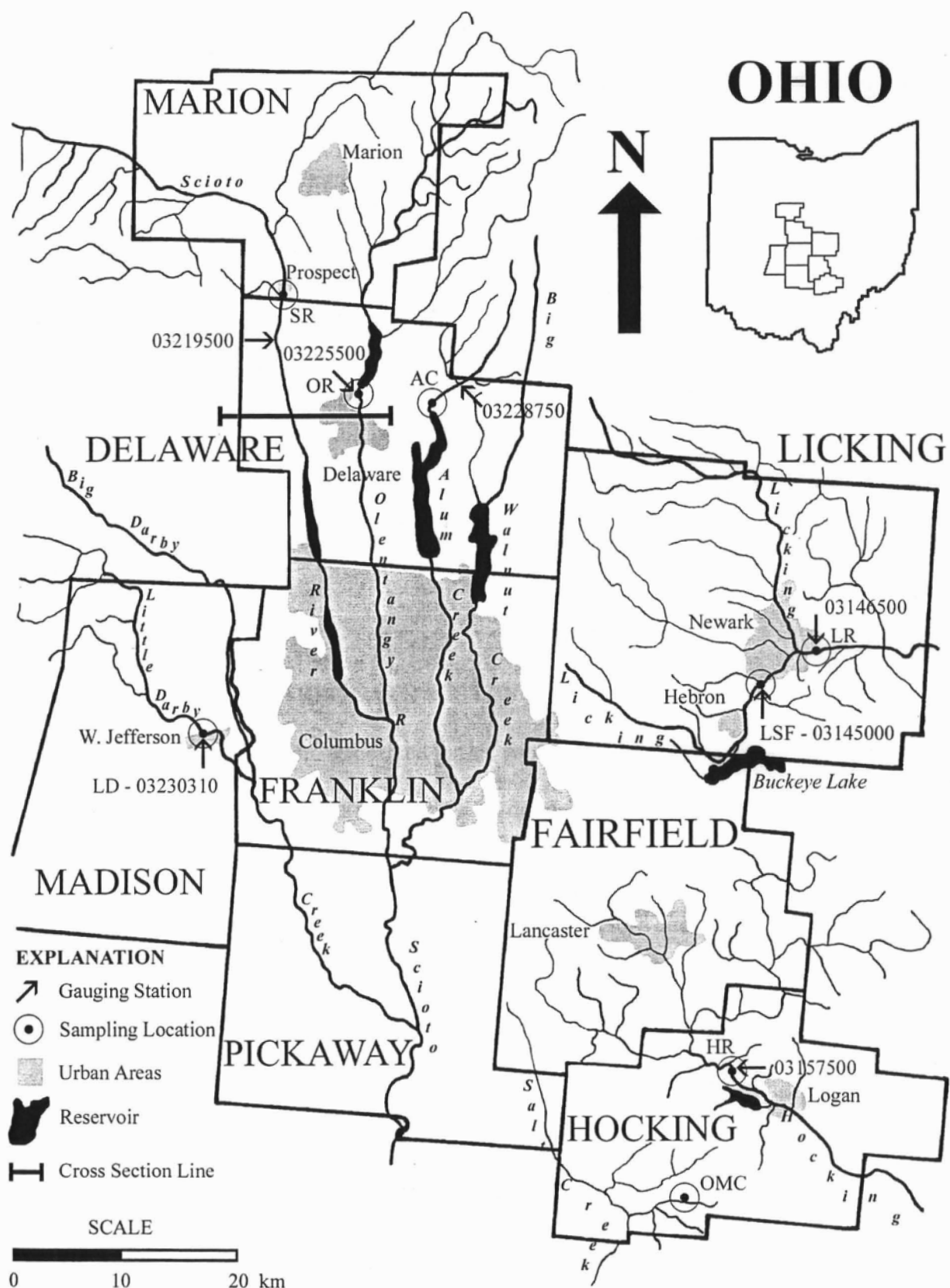
## SAMPLING AREA

The sampled streams and their drainage areas encompass a large area of central Ohio including Marion, Delaware, Madison, Licking, Fairfield, and Hocking Counties. Samples were

collected twice from eight different streams between August and October 2000 (figure 1). These sampling locations can be consolidated into two major groups with respect to their drainage areas and underlying bedrock. The four streams sampled in the Northwest portion of the sampling area are contained within bedrock consisting of limestone and shale and will be referred to as the carbonate system. The four streams sampled in the Southeast portion are generally contained within bedrock of sandstone and shale and will be referred to as the sandstone system. The geology of the sampling area will be discussed in more detail later. In general, the sampling locations were picked near active United States Geologic Survey (USGS) gauging stations in order to provide hydrologic data on the sampled streams. The sampling locations and proximal gauging stations are shown in figure 1 and listed in table 1.

**Table 1.** Sampling locations and proximal USGS gauging station.

<b>Sample</b>	<b>Stream Name (Bedrock system)</b>	<b>Location</b>	<b>USGS Gauging Station</b>
OMC	Old Man's Creek (Sandstone)	Hocking Hills State Park Old Man's Cave in Hocking County	None
LR	Licking River (Sandstone)	Stadden Bridge Rd just west of Newark in Licking County	03146500
LSF	Licking South Fork (Sandstone)	Irving Wick Dr. and S. Fork Rd. Heath in Licking County	03145000
HR	Hocking River (Sandstone)	Enterprise Rd. Enterprise in Hocking County	03157500
LD	Little Darby Creek (Carbonate)	US 40 W. Jefferson in Madison County	03230310
SR	Scioto River (Carbonate)	Market St. and Elm St. Prospect in Marion County	03219500
OR	Olentangy River (Carbonate)	Delaware Dam near US 23 Delaware in Delaware County	03225500
AC	Alum Creek (Carbonate)	US 521 Kilbourne in Delaware County	03228750



**Figure 1.** A map of the sampling area adapted from Sherman (1996).

## **GEOLOGY OF THE SAMPLING AREA**

The geology of Central Ohio is very complex and to describe it in detail goes beyond the scope of this paper. However, there are several structural and geomorphologic features in the sampling area that affect the sampled streams and their drainage areas. The most important of these include the remains of the Wisconsin and Illinoian glaciations of the Pleistocene. Figure 2 shows the extent and type of glacial deposits in the state of Ohio. These deposits, and other Quaternary deposits, vary greatly in thickness and are underlain by bedrock that is structurally influenced by the Cincinnati, Kankakee, and Findlay Arches (Swinford and Slucher, 1995; Coogan, 1996). These features allow the streams of the sampling area to be contained within many different lithologies including formations from the Silurian, Devonian and Mississippian periods.

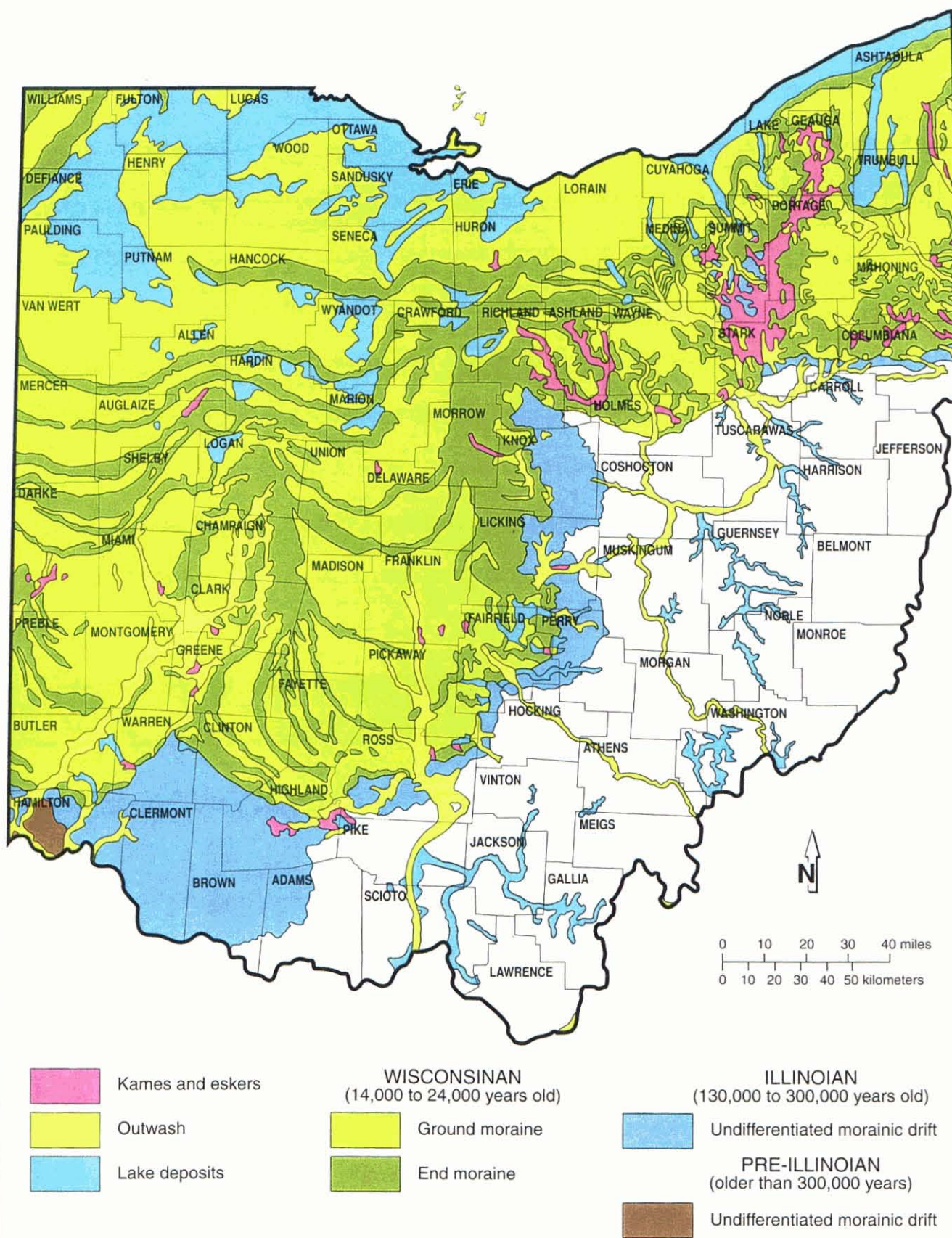
## **GEOLOGY OF THE CARBONATE SYSTEM**

The carbonate system, as defined in this paper, includes Little Darby Creek, Scioto River, Olentangy River, Alum Creek, and the principle drainage areas upstream of the sampling locations as indicated in figure 1 and table 1. The following is a brief description of the formations and lithologies that influence this system (Swinford and Slucher, 1995).

**Quaternary undifferentiated** (Pleistocene and Holocene) is dominated by glacial drift and unconsolidated gravel, sand, silt, and clay. Thickness varies from 0 to over 100 meters.

**Ohio Shale** (Upper Devonian) is dominated by carbonaceous and petroliferous shale. Included are thin beds and concretions of pyrite and sparse limestone and dolomite beds that are sparsely fossiliferous.





**Figure 2.** Glacial deposits of Ohio adapted from Coogan (1996).



**Olentangy Shale** (Middle to Upper Devonian) is dominated by pyritic shale with some occurrence of calcareous and fossiliferous shale.

**Delaware Limestone** (Middle Devonian) is dominated by microcrystalline to medium crystalline limestone with occurrences of shale and chert. Some zones contain fossils and phosphatic fish remains and minor occurrences of pyrite and conglomerates.

**Columbus Limestone** (Middle Devonian) is dominated by finely to coarsely crystalline limestone and dolomite. There are zones of abundant chert nodules and sparse shale laminae. It contains sparse fossils and some phosphatic fish remains. There is also a 5-foot bed of sandstone and a dolomite dominated pebble conglomerate at the base.

**Salina Group** including **Tymochtee Dolomite** and **Greenfield Dolomite** (Upper Silurian) is dominated by microcrystalline to medium crystalline dolomite with thin beds of shale, pyrite, limestone, and minor fragmented fossils. There are also thin zones of translucent and granular to fibrous gypsum/anhydrite associated with these formations.

**Lockport Dolomite** (Lower Silurian) is dominated by finely to coarsely crystalline dolomite with sparse shale and chert and minor occurrence of pyrite and fossils.

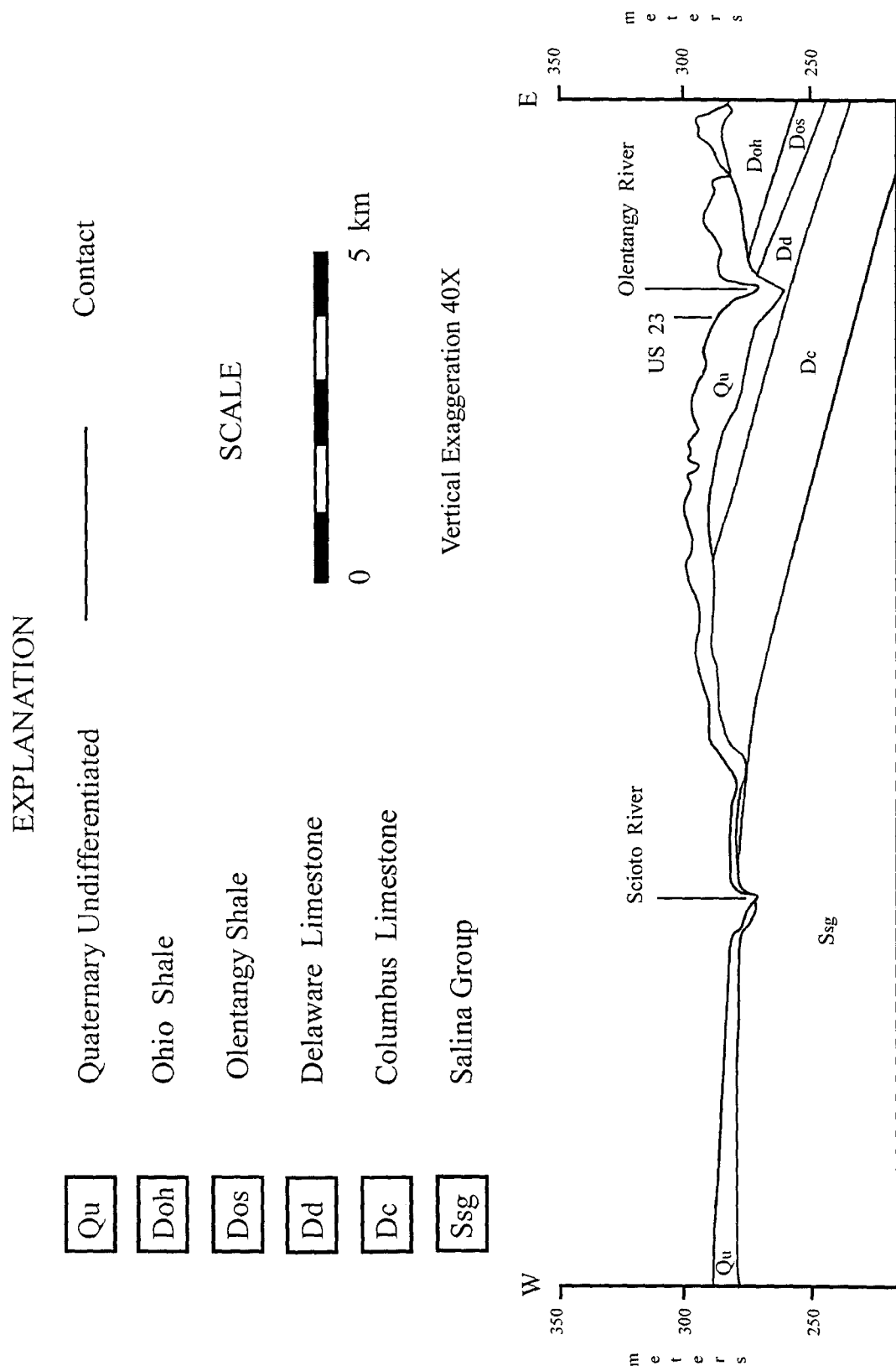
Little Darby Creek and its drainage area including several small creeks in Madison, Union, and Champaign Counties are contained within Quaternary deposits underlain by the Salina Group dolomites and Lockport Dolomite (Swinford and Slucher, 1995). Stream channels may or may not cut through the Quaternary deposits to these bedrock formations.

The Scioto River and its drainage area including the Little Scioto River in Marion County and several smaller streams in Marion, Union, and Harding Counties are contained within Quaternary deposits underlain by the Salina Group dolomites and Lockport Dolomite (Swinford and Slucher, 1995). Portions of the Little Scioto Creek and its drainage area are underlain by the Columbus Limestone and Delaware Limestone formations (Shrake, 1997). A geologic cross

section drawn through the Scioto River approximately 10 kilometers south of the sampling location (figure 3 shows that its primary river channel does in fact cut through Quaternary deposits into bedrock composed of the Salina Group dolomites (Swinford and Slucher, 1995). However, the remaining tributaries and their drainage areas may or may not cut through to the bedrock.

The Olentangy River and its drainage area including small streams in Delaware, Marion, and Morrow Counties are contained within Quaternary deposits underlain by the Ohio Shale, Olentangy Shale, Delaware Limestone, Columbus Limestone, and some shale and sandstones of the lower Waverly Series in the outermost fringes of the drainage area (Swinford and Slucher, 1995; Bownocker, 1992). This will be discussed later. A geologic cross section drawn through the Olentangy River less than 1 kilometer south of the sampling location (figure 2) shows that its primary river channel does not cut through Quaternary deposits to underlying bedrock. The remaining streams and their drainage areas may or may not cut through to the bedrock.

Alum Creek and its drainage area including a few small streams in Delaware and Morrow Counties is contained within Quaternary deposits underlain by the Ohio Shale, Olentangy Shale, and a very small portion of shale and sandstone in the lower Waverly Series in the outer most fringes of the drainage area (Bownocker, 1992). A geologic cross section drawn through Columbus, approximately 20 km south of the sampling location shows that the main channel of Alum Creek does not cut through Quaternary deposits into the bedrock (Stauffer et al, 1911).



**Figure 3.** Cross section of the carbonate system adapted from Swinford and Slucher, 1995).

## GEOLOGY OF THE SANDSTONE SYSTEM

The sandstone system, as defined in this paper, includes the Licking River, Licking South Fork, Hocking River, and Old Man's Creek, and the principal drainage areas upstream of the sampling locations as indicated in figure 1 and table 1. The bedrock underlying glacial and other Quaternary deposits in this portion of the sampling area was deposited in the Mississippian (Bownocker, 1992). The depositional environment of this area in that period ranged between marginal marine and marine; therefore bedrock lithologies encompass several different facies and vary extensively laterally throughout the sampling area (Hyde, 1953). Table 2 summarizes the Waverly Series formations, dominant lithologies, and the pertinent lithologic facies that influence this system (Hyde, 1953).

**Table 2.** Underlying bedrock of the sandstone system in the sampling area (Hyde, 1953).

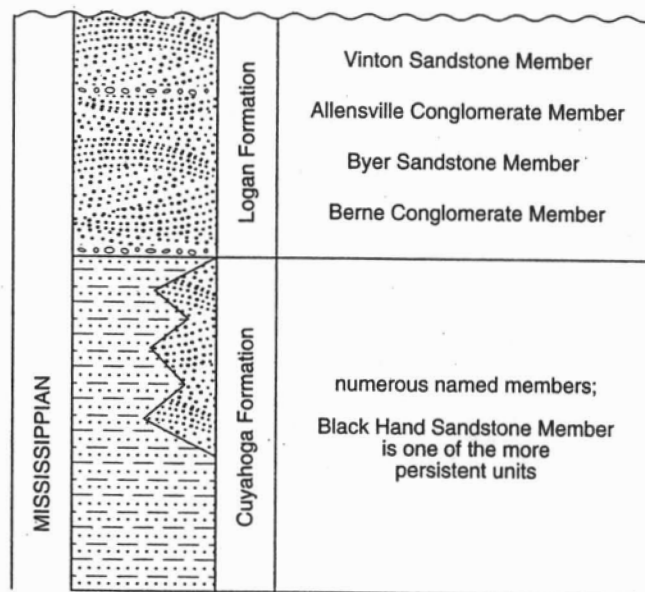
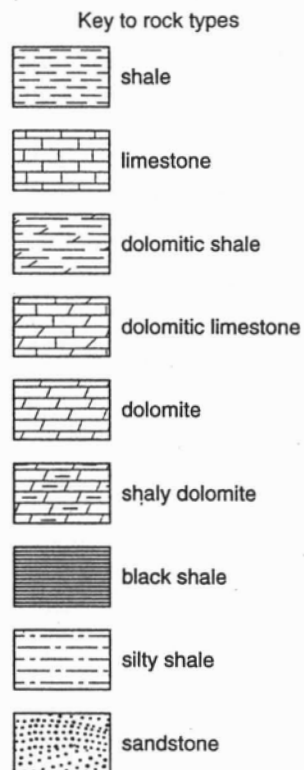
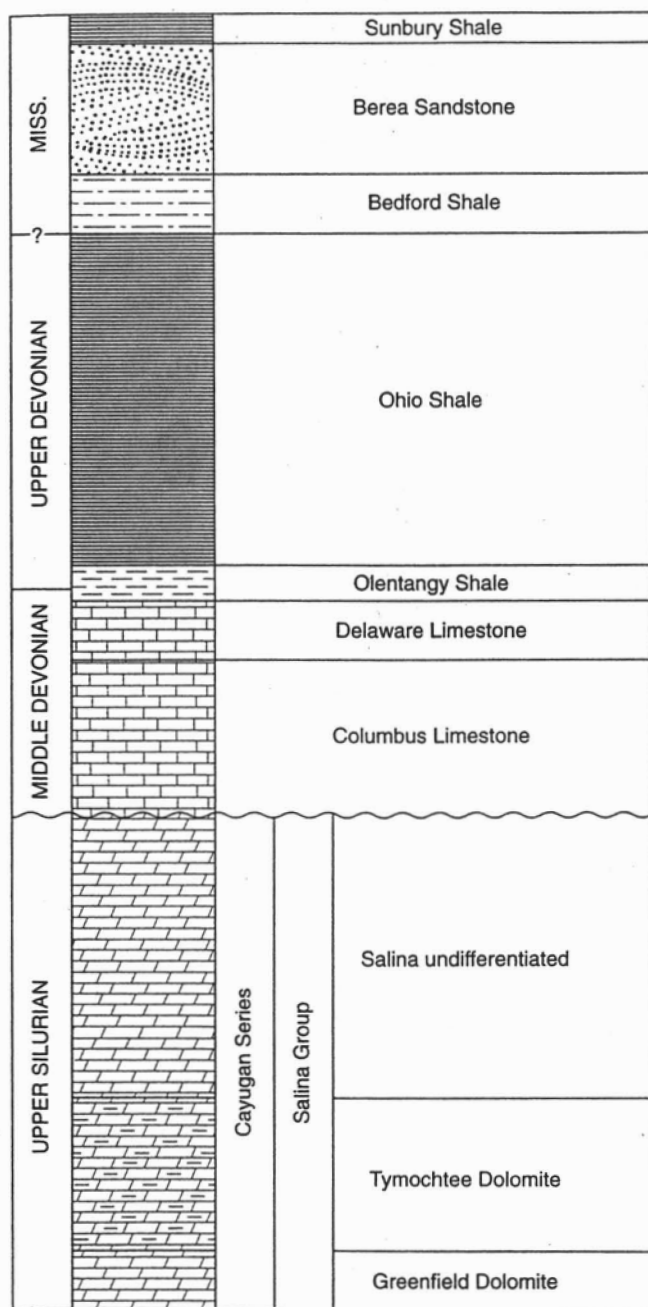
W A V E R L Y  S E R I E S	FORMATION	MEMBER	FACIES	DOMINANT LITHOLOGY
	LOGAN	Vinton		Fine sandstone and shale
		Allensville		Coarse sandstone
		Byer		Fine sandstone and sandy shale
	CUYAHOGA	Berne	Toboso	Coarse, pebbly conglomerate
			Hocking	Pebble conglomerate, coarse sandstone, and shale
		Black Hand	Toboso	Massive, coarse sandstone
			Hocking	Massive, coarse sandstone
		Fairfield	Hocking	Massive sandstone with abundant shale beds
		Lithopolis	Hocking	Thin beds of fine sandstone and gray shale
	SUNBURY SHALE			Fissile Shale
	BEREA			Sandstone and Shale
	BEDFORD SHALE			Shale and Sandstone

The Licking River, Licking South Fork, and their drainage areas including small streams in Licking, Fairfield, and Knox Counties are contained within glacial and Quaternary deposits (figure 2) underlain by the Logan and Cuyahoga formations in the Toboso facies (table 2) as defined by Hyde (1953).

The Hocking River and its drainage area including small streams in Fairfield, Hocking, and Perry Counties are contained within and overlay similar formations in the Hocking Valley facies as defined by Hyde (1953) (figure 2 and table 2).

The OMC site at Old Man's Creek and Queer Creek is contained within the Black Hand member of the Cuyahoga Formation in the Hocking Valley facies (Hyde, 1953). The creeks and their drainage areas in southern Hocking County are not affected by glacial deposits (figure 2) and cut through and over actual bedrock.

The Sunbury Shale, Berea Sandstone, and Bedford Shale formations underlie the easternmost fringes of the drainage areas in the carbonate system and do not affect the sandstone system. Generalized stratigraphic sections of bedrock underlying both systems are shown in figure 4. Although not drawn to scale, these sections show relative thickness of each formation and the rock types contained within them.



**Figure 4.** Generalized stratigraphic sections of the carbonate (left) and sandstone (right) systems showing relative thickness and rock types adapted from Coogan (1996).

## FIELD METHODS

All stream samples were collected with Nalgene brand, wide mouth, polyethylene bottles. The bottles were cleaned using the method of Welch et al (1996). Bottles used for collection and analysis of anions, silicate, alkalinity, and total suspended solids (TSS) were rinsed five times in de-ionized (DI) water, soaked in a DI water bath for approximately one week, rinsed with DI water five more times, filled with DI water, and stored at room temperature until used. Bottles used for collection and analysis of cations were cleaned using the same procedure except they were soaked in a 10% nitric acid solution for 24 hours instead of a DI water bath.

DI water (18m $\Omega$ .cm) was created using Millipore's Milli-Q™ and Rios 16 water purification system. Water traveling through this system is treated by two ion exchange columns, reverse osmosis, and is filtered for carbon and suspended matter.

Samples were collected at or near the center of the stream by a person wearing clean plastic gloves. The bottles were rinsed three times with stream water by submerging and filling the bottles upstream of where the person was standing and emptying them downstream of the collector (Welch et al, 1996). The bottles were then filled and capped while submerged and stored in a cooler of ice until returned to the laboratory. Temperature and pH of the stream were measured immediately after sample collection using a Fisher Scientific Accumet AP series handheld pH meter.

Samples were filtered on the day of collection using the method of Welch et al (1996) and were stored between 1 and 4 degrees Celsius in a laboratory refrigerator. The 0.45  $\mu$ m pore sized polycarbonate filters were used to filter approximately 50 mL of sample for each analysis of anions, cations, and silicate. Filtering equipment was rinsed five times with DI water between samples to limit contamination. Samples to be analyzed for cations were acidified to a pH of 2-3



using 20-25  $\mu$ l of Ultrex ultrapure reagent grade nitric acid (Welch et al, 1996). Anion analyses were performed on the day of collection.

Field blanks were also collected to check for contamination during transport and the quality of all apparatus. During sample collection, 2 field blanks (an acid washed bottle and a DI washed bottle) were uncapped and exposed to the air for several seconds. The bottles were capped tightly and stored in a cooler with the remainder of the samples. These blanks were treated and analyzed as samples in the laboratory.

## ANALYTICAL METHODS

Major cations and anions (Li, Na, K, Ca, Mg, Sr,  $\text{SO}_4$ , F, Cl, Br) in all the samples were analyzed by ion chromatography using a Dionex DX-120 ion chromatograph and an AS40 automated sampler that were interfaced with a computer that controlled the data using Dionex chromatography software (PeakNet) for Windows. The precision of these measurements was less than  $\pm 10\%$ .

Silicate-silica analyses were performed by colorimetric analysis (Mullin and Riley, 1955; Strickland and Parsons, 1972). For analysis, 20 mL of sample, diluted by a factor of 2 with DI water, 3 mL of acid ammonium molybdate, 15 mL of reducing agent, and 12 mL of DI water are put into a 60 mL DI washed bottle and stored at room temperature for 24 hours. The reducing agent consists of 400 mL of 25% sulfuric acid, 330 mL of filtered metol sulfite, 4 g of anhydrous sodium sulfite, 6.6 g of *p*-methylamino-phenol-sulfate, 2000 mL of 60% oxalic acid, and 70 mL of DI water. The 500 mL of acid ammonium molybdate solution consists of 30 mL concentrated HCl, 10 g of ammonium molybdate, and 470 mL of DI water. A Milton Roy Spectronic 501 series spectrometer set to a wavelength of 812 nm measures the absorbance of the sample

mixture in a 1 cm optical cell. Silica concentration was calculated from an equation derived from the trend line of an absorbance over concentration graph using a set of standard solutions.

Alkalinities were determined by titration of 20 mL of each sample with 0.1N HCl to a pH of 4.5 using an Orion model 720A pH meter. Titrations were performed immediately upon return to the laboratory.

Total suspended solids (TSS) in the samples were determined gravimetrically. For each sample, 300 - 400 mL was filtered through a cellulose acetate filter of pore size 0.45  $\mu\text{m}$  and placed in an oven at 40 degrees Celsius for drying. The filters were periodically removed from the oven and cooled in a plastic Nalgene brand desiccater and weighed using a Mettler Toledo AB104-S balance. The filters were weighed every few days until a constant weight was reached.

Geochemical modeling was conducted using PHREEQE (Parkhurst et al, 1990), a USGS computer program used for determining geochemical equilibria. This program calculates the value of over-saturation of many different rock type phases taking into account all ion data collected, pH, temperature, and total carbon.

## GEOCHEMISTRY

There are many environmental and anthropogenic factors that affect the chemistry of natural waters. Major environmental factors affecting the sampling area include rock type, rainfall and atmospheric chemistry, groundwater chemistry, soil, and vegetation. The sampling area is influenced by a myriad of anthropogenic sources ranging from industry in urban areas and agriculture in rural ones. To explain how all of these factors influence water chemistry goes beyond the scope of this paper. The results of the testing in this project focus on the water chemistry of the dissolved load and will be targeted with respect to the chemical weathering of specific rock types. In order to understand the influence of geology it is important to understand how minerals react with natural waters. Table 3 lists the most abundant minerals involved in chemical weathering in the sampling area.

**Table 3.** Common minerals and their reactions to weathering (Berner and Berner, 1996).

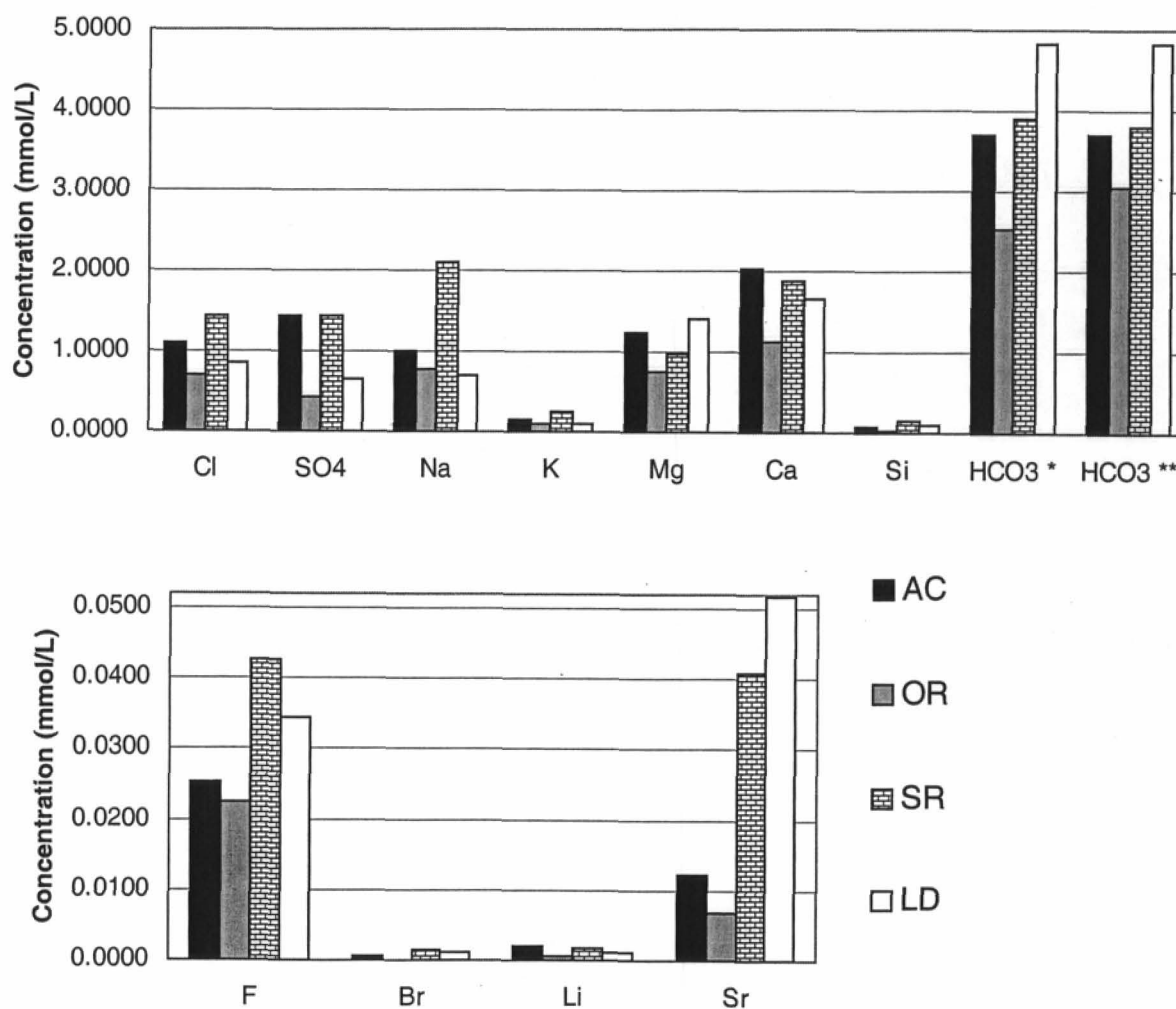
MINERAL	FORMULA	PRINCIPAL REACTIONS
Calcite	$\text{CaCO}_3$	$\text{H}_2\text{CO}_3 + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$
Aragonite		$\text{H}_2\text{SO}_4 + 2 \text{CaCO}_3 \rightarrow 2\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{HCO}_3^-$
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	$2\text{H}_2\text{CO}_3 + \text{CaMg}(\text{CO}_3)_2 \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^-$ $2\text{H}_2\text{SO}_4 + 2\text{CaMg}(\text{CO}_3)_2 \rightarrow 2\text{Ca}^{2+} + 2\text{Mg}^{2+} + 2\text{SO}_4^{2-} + 4\text{HCO}_3^-$
Pyrite <i>From Shale</i>	$\text{FeS}_2$	$4 \text{FeS}_2 + 15\text{O}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{H}_2\text{SO}_4$ <i>Sulfuric acid then reacts with other minerals</i>
Halite	$\text{NaCl}$	$\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$ <i>Congruent dissolution by <math>\text{H}_2\text{O}</math></i>
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaSO}_4 \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$
Anhydrite	$\text{CaSO}_4$	<i>Congruent dissolution by <math>\text{H}_2\text{O}</math></i>
Quartz	$\text{SiO}_2$	<i>Is resistant to weathering but occurs as <math>\text{H}_4\text{SiO}_4</math> in dissolved load from secondary minerals such as Talc and Kaolinite</i>
K-Feldspar Plagioclase	$\text{KAlSi}_3\text{O}_8$ $\text{NaAlSi}_3\text{O}_8$	$2\text{KAlSi}_3\text{O}_8 + 2\text{H}^+ + 9\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ + 4\text{H}_4\text{SiO}_4$ <i>Kaolinite ↓</i>
Carbonic Acid	$\text{H}_2\text{CO}_3$	$\text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}_2\text{CO}_3$

# CARBONATE SYSTEM

## RESULTS

Figure 5 compares the average concentrations (mmol/L) of each sampling location within the carbonate system. In general all four sampled streams have trends similar in their predominant and minor ions and their ratios. However, AC, SR, and LD have somewhat higher concentrations than OR for all ions.

**Figure 5.** Ionic concentrations of the carbonate system averaged over two dates.



\* Results determined by alkalinity titration

\*\* Results determined by charge balance

**Table 4.** Molar concentrations (mmol/L) of ions and TSS (mg/L) in the carbonate system.

DATE	29 AUGUST 2000				29 SEPTEMBER 2000			
SAMPLE	AC	OR	SR	LD	AC	OR	SR	LD
TEMP °C	21.7	23.1	21.8	21.8	11.0	15.0	13.4	13.0
PH	8.01	7.65	7.66	8.19	7.94	7.04	7.55	7.87
F <sup>-</sup>	0.0353	0.0305	0.0622	0.0436	0.0151	0.0144	0.0230	0.0250
Cl <sup>-</sup>	0.9978	0.8907	1.7847	0.8148	1.2093	0.5317	1.0699	0.8690
Br <sup>-</sup>	ND	ND	0.0030	0.0020	0.0010	ND	ND	ND
SO <sub>4</sub> <sup>2-</sup>	1.5607	0.5498	1.6471	0.6450	1.2680	0.3090	1.2177	0.6623
Li <sup>+</sup>	0.0020	0.0010	0.0020	0.0010	0.0018	ND	0.0014	0.0011
Na <sup>+</sup>	0.9523	0.7333	3.1060	0.6615	1.0329	0.8247	1.0917	0.7365
K <sup>+</sup>	0.1271	0.0991	0.2864	0.0826	0.1613	0.1009	0.1935	0.1144
Mg <sup>2+</sup>	1.2574	0.7678	1.0187	1.4746	1.1722	0.7327	0.9538	1.3063
Ca <sup>2+</sup>	1.9880	1.2235	1.8205	1.6865	2.0666	1.0270	1.9212	1.6385
Sr <sup>2+</sup>	0.0122	0.0068	0.0480	0.0533	0.0120	0.0070	0.0339	0.0499
Silica	0.0582	0.0252	0.1368	0.1042	0.0996	0.0367	0.1556	0.1133
HCO <sub>3</sub> <sup>-</sup> (titration)	3.5275	2.7400	4.4625	4.9450	3.8650	2.3100	3.3275	4.6925
HCO <sub>3</sub> <sup>-</sup> (charge)	3.4402	2.8076	4.0257	5.0243	3.9354	3.2948	3.5746	4.6217
TSS	14.00	24.00	35.00	70.50	36.00	28.00	7.75	14.50

ND Not detected above detection limit listed in Table 7A in the appendix

The results of laboratory analyses of the carbonate system are listed in table 4.

Temperature and pH at the time of collection are also listed. Places where no value is recorded were below the limit of detection of the ion chromatograph. The limit of detection for each analyte is listed in the appendix in table 7A. Table 5 below contains molar ratios of certain ions.

**Table 5.** Molar ratios of some ions in the carbonate system.

Sample	$\text{HCO}_3^- : \text{Ca}^{2+} : \text{Mg}^{2+} : \text{SO}_4^{2-}$	$\text{Na}^+ : \text{Cl}^-$
AC	4 : 2 : 1 : 1	1 : 1
OR	6 : 2 : 2 : 1	1 : 1
SR	4 : 2 : 1 : 1	1 : 1
LD	~ 5 : 1.5 : 1.5 : 0.5	1 : 1

Geochemical modeling results for the carbonate system are recorded in table 8A in the appendix. The results of these models suggest that the geochemistry of AC is dominated by the phases (rock type) of dolomite, calcite, and aragonite; OR by calcite and dolomite; SR by dolomite, calcite, quartz, and aragonite; LD by dolomite, calcite, aragonite, strontianite, quartz, and talc.

## DISCUSSION

All sampled streams within the carbonate system are dominated by bicarbonate ( $\text{HCO}_3^-$ ). In addition their major ion molar ratios, in conjunction with geochemical modeling results, provide good evidence suggesting which rock types are being weathered and by what process.

Results of geochemical modeling suggest that the major rock types being weathered by natural waters in AC and SR are dolomite, calcite, and aragonite. A ratio of molar concentrations of ( $\text{HCO}_3^- : \text{Ca}^{2+} : \text{Mg}^{2+} : \text{SO}_4^{2-}$ ) equal to 4:2:1:1 corroborates this and further suggests that these rock types underwent chemical weathering dominated by both sulfuric acid

derived from shale and carbonic acid. The presence of  $\text{Sr}^{2+}$  at a concentration around 0.01 mmol/L in AC and 0.04 mmol/L in SR most likely occurs as a product of the replacement of  $\text{Ca}^{2+}$  and implies the presence of aragonite in both AC and SR but of more aragonite in SR than in AC. The geology of the carbonate system does not suggest the presence of large amounts of evaporite minerals including halite ( $\text{NaCl}$ ). Sources for the occurrence of  $\text{Na}^+$  and  $\text{Cl}^-$  include cyclic salt in rain and dry fall out, salts that may be dispersed in shale thought to be trapped at the time of deposition (Drever, 1988), and several anthropogenic sources including sewage, mining, and road salt (Berner and Berner, 1996).

Geochemical models of SR suggest quartz as an additional rock type being weathered. However, in addition to having the highest silica concentration of the system SR also contains the highest  $\text{K}^+$  and higher  $\text{Na}^+$  concentrations. Because quartz is resistant to weathering, the presence of these ions can be attributed to the weathering of K-feldspar ( $\text{KAlSi}_3\text{O}_8$ ), plagioclase ( $\text{NaAlSi}_3\text{O}_8$ ), secondary minerals like kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), and other silicate minerals composing sedimentary, metamorphic, and igneous rocks found in glacial till. However, this cannot be proven because this project did not collect data on trace metal concentrations including aluminum ( $\text{Al}^{3+}$ ). Therefore all results of geochemical modeling that report an over-saturation of the quartz phase must be viewed objectively and the presence and weathering of these additional minerals seriously considered. However, as described earlier, the carbonate rocks in this area do contain abundant quartz in the form of chert and contained in shale.

Geochemical models of OR suggest that the major rock types involved in weathering include calcite and dolomite. A ratio molar concentrations of ( $\text{HCO}_3^- : \text{Ca}^{2+} : \text{Mg}^{2+} : \text{SO}_4^{2-}$ ) equal to 6:2:2:1 also suggests that these rock types were attacked by carbonic acid more so than by sulfuric acid. Calcite and dolomite attacked by carbonic acid alone would impart a ratio of 6:2:1:0. In addition to weathering by sulfuric acid, higher concentrations of  $\text{Mg}^{2+}$  and  $\text{SO}_4^-$  could



be attributed to various Mg-silicates that can occur in the rocks of the glacial till and anthropogenic sources respectively. Concentrations of  $K^+$  and silica in OR are very low. The low silica concentration could possibly be attributed to particle removal behind the dam. The presence of  $K^+$  in this case is not from minerals mentioned before but more likely can be attributed to anthropogenic and biogenic sources including fertilizer (Berner and Berner, 1996). Much lower concentrations of  $Sr^{2+}$  also suggest small amounts or no aragonite present. Concentrations of all ions in OR are substantially lower than the rest of the carbonate system. The exact cause of this is not clearly known but can be attributed to the Delaware dam located immediately upstream of the sampling location.

Geochemical models of LD suggest that dolomite, calcite, and aragonite, quartz, talc, and strontianite are being weathered. The molar ratios in this sample do not clearly suggest what drives the weathering of these rock types. It is logical to assume that some combination of carbonic and sulfuric acid are involved.  $Sr^{2+}$  concentrations are highest in LD, about 0.05 mmol/L, and clearly suggest a strong influence of aragonite and possibly strontianite. Moderate concentrations of  $K^+$  and silica can be attributed to the same sources and considerations of SR discussed earlier. Talc and other Mg-silicates can be additional sources of  $Mg^{2+}$ .

The presence of  $F^-$ ,  $Li^+$ , and  $Br^-$  in all the samples of the carbonate system can be attributed to anthropogenic sources.

TSS data showed no discernable patterns in respect to the two dates of collection. Reasons for fluctuation of TSS in a given sample over two dates can be attributed to fluctuations of precipitation and flow conditions. With respect to field observations during collection, it is reasonable to assume that during periods of greater precipitation, which is conducive to higher flow conditions, a higher amount of particulate matter is present in the suspended load of streams.

## CONCLUSION

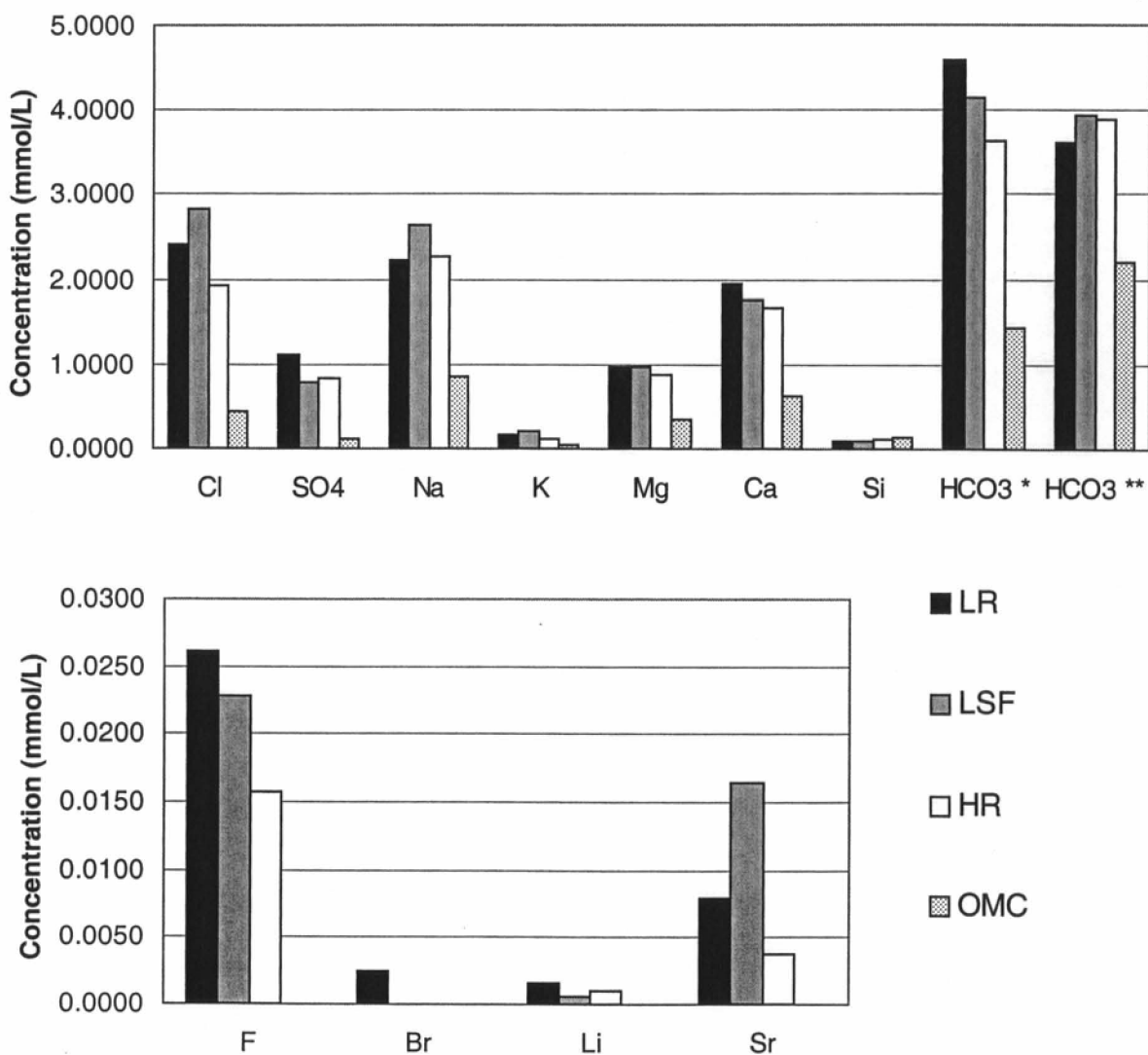
Results of the four sampling locations in the carbonate system AC, OR, SR, and LD suggest that the chemistry of these natural waters is predominantly controlled by bedrock and surficial geology. Furthermore, ionic concentrations reflect the specific rock types that are being weathered and suggest by what process this occurs. As discussed earlier these results suggest that calcite and dolomite are the dominant rock type being weathered and that minerals such as aragonite, quartz, and several secondary minerals also contribute to the chemistry of these waters. These results are all consistent with the geology of the carbonate system described previously. Anthropogenic and other sources of major and minor ions found appear to be subordinate to the effect of bedrock and surficial geology in the system.

## SANDSTONE SYSTEM

### RESULTS

In general LR, LSF, and HR have trends similar in their respect to predominant and minor ions and their ratios. However, OMC differs considerably from the rest of the system. It consistently contains substantially lower concentrations of all major and minor constituents with the exception of silica. Results are listed in table 5.

**Figure 6.** Ionic concentrations of the sandstone system averaged over two dates.



**Table 6.** Molar concentrations (mmol/L) of ions and TSS (mg/L) in the sandstone system.

DATE	23 AUGUST 2000				04 OCTOBER 2000			
SAMPLE	LSF	LR	HR	OMC	LSF	LR	HR	OMC
TEMP °C	20.6	21.6	21.5	18.7	17.4	19.0	18.3	15.0
PH	8.00	7.93	8.17	7.93	8.06	7.93	8.12	7.78
F <sup>-</sup>	0.0252	0.0362	0.0199	ND	0.0204	0.0160	0.0115	ND
Cl <sup>-</sup>	3.4228	2.6437	2.2335	0.7320	2.2154	2.1489	1.6310	0.1331
Br <sup>-</sup>	ND	0.0008	ND	ND	ND	0.0042	ND	ND
SO <sub>4</sub> <sup>2-</sup>	0.8275	1.0853	0.9825	0.1925	0.7294	1.1374	0.6668	0.0350
Li <sup>+</sup>	ND	ND	ND	ND	0.0013	0.0033	0.0020	ND
Na <sup>+</sup>	2.3754	2.8948	2.1775	0.7121	2.8983	1.5465	2.3809	0.9848
K <sup>+</sup>	0.1413	0.2490	0.0996	0.0557	0.2552	0.0882	0.1448	0.0548
Mg <sup>2+</sup>	0.8961	1.0792	0.8554	0.3331	1.0595	0.8718	0.8975	0.0019
Ca <sup>2+</sup>	1.6632	1.9678	1.5493	0.6223	1.8452	1.9404	1.7784	0.6280
Sr <sup>2+</sup>	0.0204	0.0084	0.0037	ND	0.0124	0.0076	0.0038	ND
Silica	0.0829	0.1016	0.1267	0.1194	0.0942	0.0934	0.1124	0.1416
HCO <sub>3</sub> <sup>-</sup> (titration)	4.4900	4.5450	3.7150	1.5200	3.8075	4.6150	3.5600	1.3625
HCO <sub>3</sub> <sup>-</sup> (charge)	2.5731	4.4032	2.8679	1.5616	5.2943	2.8337	4.9109	2.8309
TSS	14.75	8.25	2.00	35.00	11.00	6.75	59.75	11.25

ND Not detected above detection limit listed in Table 7A in the appendix

**Table 7.** Molar ratios of some ions in the sandstone system.

Sample	$\text{HCO}_3^- : \text{Ca}^{2+} : \text{Mg}^{2+} : \text{SO}_4^{2-}$	$\text{Na}^+ : \text{Cl}^-$
LR	4 : 2 : 1 : 1	1 : 1
LSF	4 : 2 : 1 : 1	1 : 1
HR	4 : 2 : 1 : 1	1 : 1
OMC	<i>Not clear however</i> $\text{Silica} : \text{K}^+ = 2 : 1$	2 : 1

Geochemical modeling results for the sandstone system are recorded in table 9A in the appendix. These models suggest that the geochemistry of LSF is dominated by the weathering of dolomite, calcite, aragonite, talc, and quartz; LR by dolomite, calcite, aragonite, and quartz; HR by dolomite, calcite, aragonite, talc, and quartz; OMC by quartz alone.

## DISCUSSION

The sampled streams in the sandstone system are also dominated by  $\text{HCO}_3^-$ . Subordinate and minor ions and their molar ratios in conjunction with geochemical modeling results provide good evidence suggesting which rock types are being weathered and by what process.

Results of geochemical modeling suggest that the major rock types being weathered by natural waters in LSF, LR, and HR are dolomite, calcite, aragonite, and quartz. Ratios of molar concentrations of  $(\text{HCO}_3^- : \text{Ca}^{2+} : \text{Mg}^{2+} : \text{SO}_4^{2-})$  equal to 4:2:1:1 corroborates this and like the carbonate system also suggests that these rock types underwent chemical weathering dominated by both sulfuric acid derived from shale and carbonic acid. The presence of  $\text{Sr}^{2+}$  in all three of these samples also suggests that there has been replacement of  $\text{Ca}^{2+}$  and implies the presence of aragonite. The geology of the sandstone system does not include large amounts of evaporite minerals like halite ( $\text{NaCl}$ ). Therefore the presence of  $\text{Na}^+$  and  $\text{Cl}^-$  in the samples can be attributed to the same sources mentioned in the carbonate system samples. However, it is

important to mention that LSF, LR, and HR sample were collected near urban areas. Therefore sources of these ions also include anthropogenic ones. Geochemical modeling results suggesting quartz as an additional phase in addition to the occurrence of  $K^+$  and  $Na^+$  should be viewed objectively and under the same considerations discussed in the carbonate system with respect to the likely weathering of K-feldspar, plagioclase, secondary minerals, and other silicate minerals found in the glacial till.

Geochemical modeling results of OMC suggest that quartz is the only rock type being weathered. This again should be viewed objectively and under the same considerations just stated above. However, ratios of molar concentrations of other ions provide further evidence for which rock types are being weathered. Ratios of molar concentrations of (Silica :  $K^+$ ) equal to 2 : 1 and ( $Na^+$  :  $Cl^-$ ) equal to 2 : 1 suggest that K-feldspar and plagioclase are also being weathered. However, it is difficult to prove without aluminum data.

Results of OMC are considerably different from the remaining three samples of the sandstone system. OMC concentrations of all constituents are substantially lower, with the exception of silica. OMC contains no  $Sr^{2+}$ . All of these results can be attributed to the dominance of sandstone in the bedrock and lack of surficial deposits including glacial till. The drainage area of this sample is considerably smaller than the other sampled streams of both systems, suggesting that less residence time of water in the systems results in less weathering and less dissolved load in the stream.

The presence of  $F^-$ ,  $Li^+$ , and  $Br^-$  in all the samples of the carbonate system can be attributed to anthropogenic sources.

TSS data showed no discernable patterns in respect to the two dates of collection.

## CONCLUSION

The sampled streams of the sandstone system can be separated into two groups. Results of sampling locations LR, LSF, and HR suggest that the chemistry of these natural waters is controlled by surficial and bedrock geology. Major and minor element concentrations in conjunction with geochemical modeling suggest that dolomite and calcite are the dominant rock types being weathered and that aragonite, quartz, and secondary minerals also contribute to the chemistry of these waters. These results are consistent with the surficial geology described previously.

Results from OMC suggest that the water chemistry is strongly controlled by bedrock. Quartz and perhaps K-feldspar and plagioclase are the dominant minerals being weathered. These results are also consistent with the geology of this portion of the sandstone system and should be more indicative of how sandstone bedrock affects natural water chemistry in temperate climates.



## SUMMARY OF CONCLUSIONS

Figure 7. Average concentrations of both systems and OMC.

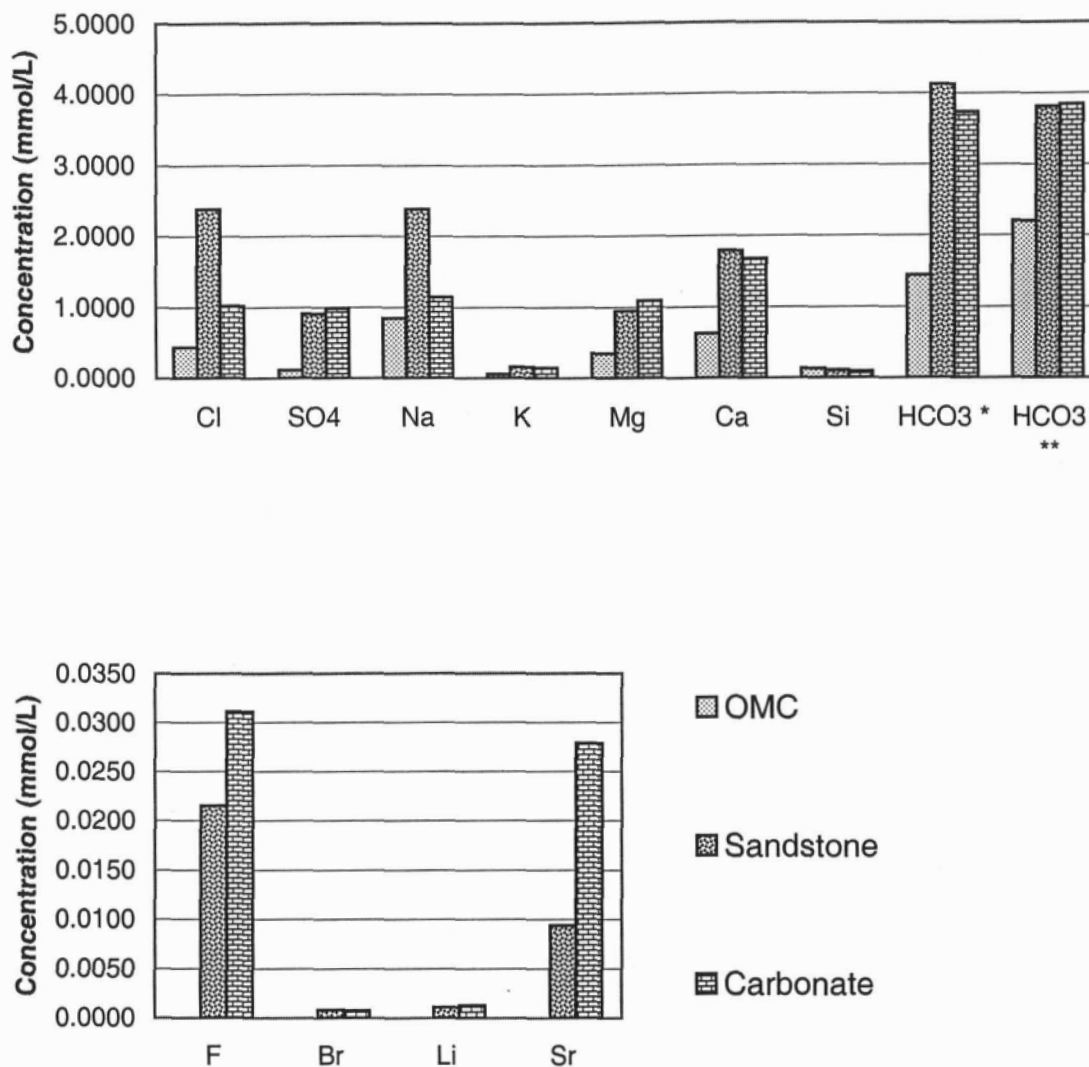


Figure 7 shows the average molar concentration (mmol/L) of both systems and OMC over both sampling dates. These results, in conjunction with geochemical modeling, clearly show that the carbonate system and the sandstone system, excluding OMC, have similar water chemistry. The higher concentrations of Na<sup>+</sup> and Cl<sup>-</sup> ions as well as the differences in

concentration of other ions can be attributed to the extent of anthropogenic influence. Higher concentrations of  $K^+$  in the sandstone system suggest more weathering of secondary minerals and other aluminosilicates. Both systems are dominated by bicarbonate and contain ions derived chiefly from the weathering of carbonate minerals. However, higher concentrations of  $Sr^{2+}$  in the carbonate system suggest a stronger influence of carbonate minerals than in the sandstone system.

Results of OMC are significantly different and should be considered separately. Molar concentrations of all constituents are substantially lower with the exception of silica, which is higher than both the sandstone and carbonate system averages. Although the water chemistry of OMC appears to be dominated by bicarbonate it contains a much higher concentration of silica proportionally with bicarbonate when compared to the other two systems. This can be attributed to the weathering of silicate and secondary minerals derived from sandstone.

Results of this study have shown that the chemistry of natural waters found in the streams of central Ohio are primarily controlled by the chemical weathering of different rock types found in bedrock and surficial geology. Both systems are strongly influenced by the limestone, dolomite, and shale dominated bedrock and glacial material. The sandstone system appears to be further influenced by the abundant sandstone found in underlying bedrock. OMC is influenced by sandstone and shale dominated bedrock. It has also shown that environmental and anthropogenic sources both rural and urban additionally affect the water chemistry but are subordinate to the effects of the geology.

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## APPENDIX



**Table 1A.** Colorimetric Analysis (AUG).

Sample	Dilution	Conc.	Absorbance	Calc.	Si mg/L	mmol/L
blank	1	0	0	-0.00487	-0.00487	-0.00017
standard 0.05mg/L	1	0.05	0.017	0.04691	0.04691	0.00167
standard 0.1mg/L	1	0.1	0.034	0.09869	0.09869	0.00351
standard 0.2mg/L	1	0.2	0.068	0.20225	0.20225	0.00720
standard 0.5mg/L	1	0.5	0.168	0.50685	0.50685	0.01804
standard 1.0mg/L	1	1	0.331	1.00335	1.00335	0.03572
standard 2.0mg/L	1	2	0.657	1.99634	1.99634	0.07107
Field Blank 29 Aug 00	1		0	-0.00487	-0.00487	-0.00017
AC 29 Aug 00	2		0.270	0.81754	1.63509	0.05821
OR 29 Aug 00	2		0.118	0.35455	0.70911	0.02524
SR 29 Aug 00	4		0.317	0.96071	3.84283	0.13680
LD 29 Aug 00	2		0.482	1.46330	2.92659	0.10419
Field Blank 23 Aug 00	1		0	-0.00487	-0.00487	-0.00017
HR 23 Aug 00	2		0.586	1.78008	3.56016	0.12674
LR 23 Aug 00	2		0.470	1.42674	2.85349	0.10158
LSF 23 Aug 00	2		0.384	1.16479	2.32958	0.08293
OMC 23 Aug 00	2		0.552	1.67652	3.35303	0.11937

#### SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.99998
R Square	0.99996
Adjusted R Square	0.99996
Standard Error	0.00155
Observations	7

#### ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	0.34326	0.34326	142651.3	2.4693E-12
Residual	5	1.2E-05	2.40628E-06		
Total	6	0.34327			

	<i>Coefficients</i>	<i>Std Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>
Intercept	0.00158	0.00076	2.0938	0.09046	-0.00036	0.00353
X Variable 1	0.32829	0.00087	377.69	2.4693E-12	0.32605	0.33052

**Table 2A.** Colorimetric Analysis (OCT).

Sample	Dilution	Conc.	Absorbance	Calc.	Si mg/L	mmol/L
blank	1	0	0	-0.00182	-0.00182	-0.00006
standard 0.05mg/L	1	0.05	0.016	0.04681	0.04681	0.00167
standard 0.1mg/L	1	0.1	0.033	0.09848	0.09848	0.00351
standard 0.2mg/L	1	0.2	0.066	0.19878	0.19878	0.00708
standard 0.5mg/L	1	0.5	0.167	0.50578	0.50578	0.01801
standard 1.0mg/L	1	1	0.332	1.00729	1.00729	0.03586
standard 2.0mg/L	1	2	0.657	1.99514	1.99514	0.07103
Field Blank 29 Aug 00	1		0	-0.00182	-0.00182	-0.00006
AC 29 Aug 00	2		0.461	1.39939	2.79878	0.09964
OR 29 Aug 00	2		0.17	0.51489	1.02979	0.03666
SR 29 Aug 00	4		0.36	1.09240	4.36960	0.15556
LD 29 Aug 00	2		0.524	1.59088	3.18176	0.11327
Field Blank 23 Aug 00	1		0	-0.00182	-0.00182	-0.00006
HR 23 Aug 00	2		0.52	1.57872	3.15745	0.11240
LR 23 Aug 00	2		0.432	1.31125	2.62249	0.09336
LSF 23 Aug 00	2		0.436	1.32340	2.64681	0.09423
OMC 23 Aug 00	2		0.655	1.98906	3.97812	0.14162

#### SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.99998
R Square	0.99996
Adjusted R Square	0.99996
Standard Error	0.00155
Observations	7

#### ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	0.34326	0.34326	142651.3	2.4693E-12
Residual	5	1.2E-05	2.40628E-06		
Total	6	0.34327			

	<i>Coefficients</i>	<i>Std Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>
Intercept	0.00158	0.00076	2.0938	0.09046	-0.00036	0.00353
X Variable 1	0.32829	0.00087	377.69	2.4693E-12	0.32605	0.33052

**Figure 1A.** Graphs of colorimetric (silica) standard solutions determining concentration equations.

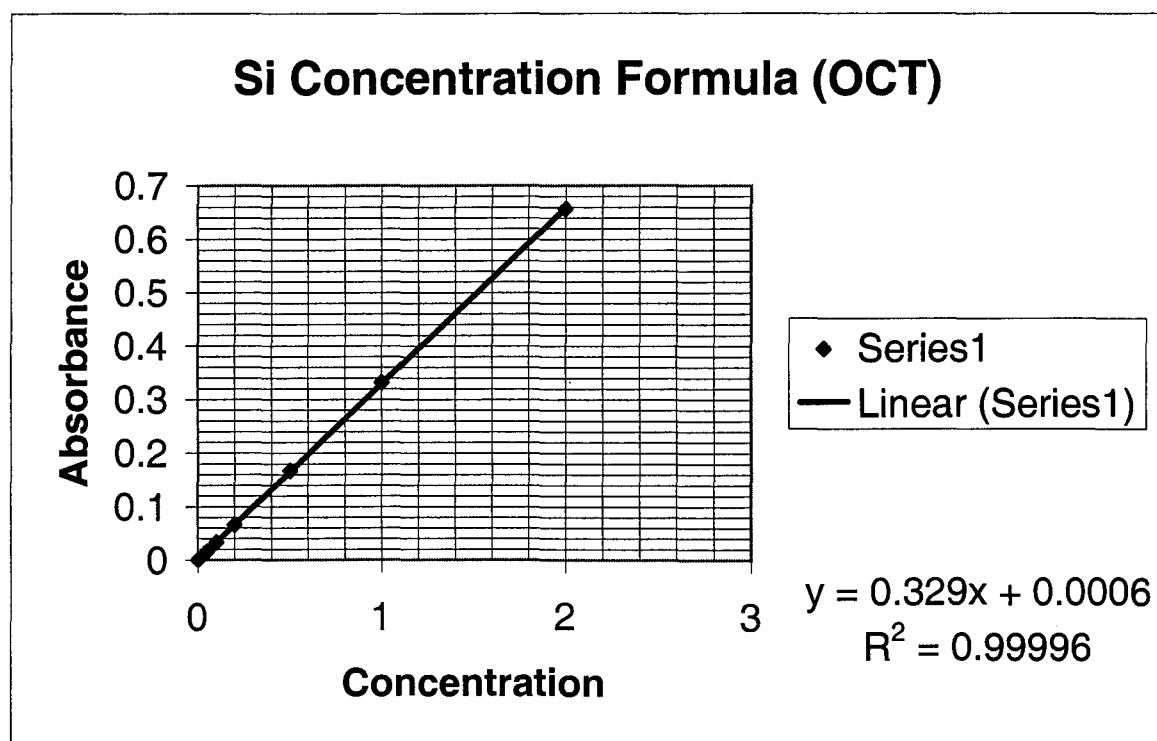
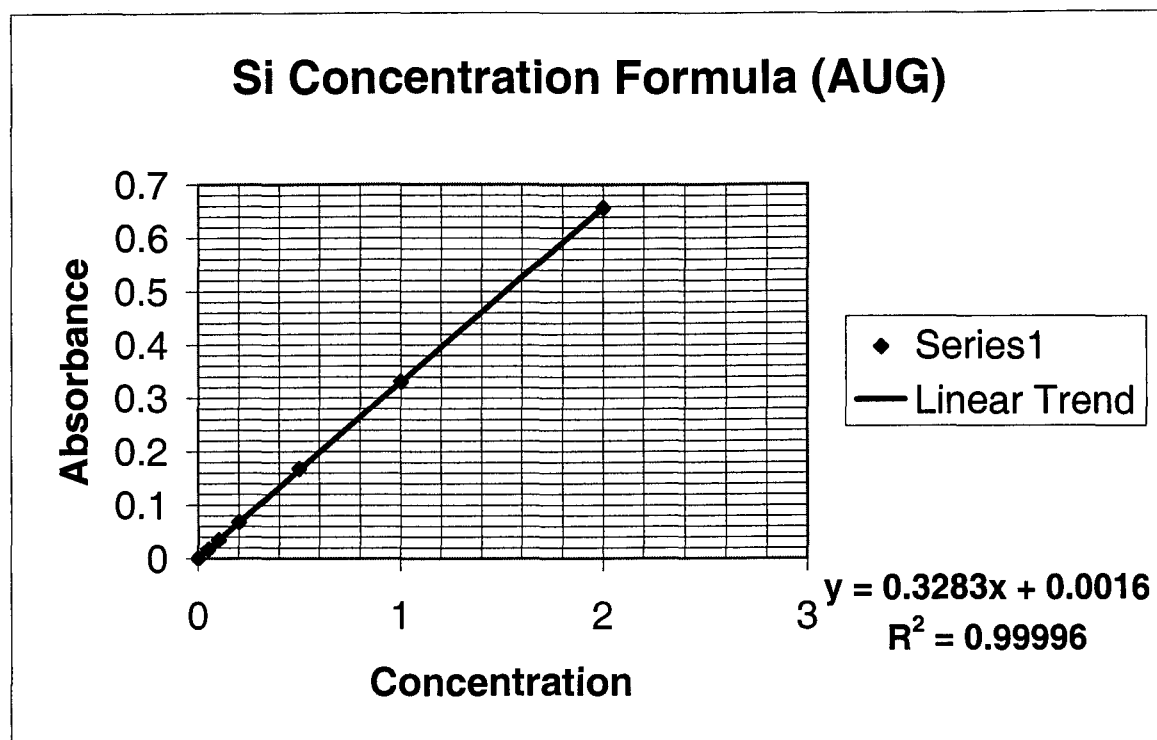


Table 3A. TSS data (August - September)

Sample	initial filter weight after 3 days in oven	volume of sample mL	filter+sample days in oven	mg/L	filter+sample days in oven	mg/L	filter+sample days in oven	mg/L	filter+sample days in oven	mg/L	filter+sample days in oven	mg/L	filter+sample days in oven	mg/L
HR	0.0857 8/24/2000	400	0.0901 1	11.00	0.0895 6	9.50	0.0894 14	9.25	0.0875 19	4.50	0.0866 28	2.25	0.0865 32	2.00
LSF	0.0870 8/24/2000	400	0.0959 1	22.25	0.0953 6	20.75	0.0949 14	19.75	0.0938 19	17.00	0.0929 28	14.75	0.0929 32	14.75
OMC	0.0860 8/24/2000	400	0.1029 1	42.25	0.1024 6	41.00	0.1017 14	39.25	0.1004 19	36.00	0.1000 28	35.00	0.0995 32	33.75
LR	0.0868 8/25/2000	400	0.0929 1	15.25	0.0928 6	15.00	0.0921 14	13.25	0.0909 19	10.25	0.0902 28	8.50	0.0901 32	8.25
AC	0.0846 9/7/2000	400	0.0931 1	21.25	0.0917 7	17.75	0.0910 12	16.00	0.0905 14	14.75	0.0902 43	14.00		
OR	0.0837 9/7/2000	300	0.0939 1	34.00	0.0924 7	29.00	0.0918 12	27.00	0.0915 14	26.00	0.0909 43	24.00		
SR	0.0822 9/8/2000	300	0.0939 6	39.00	0.0939 11	39.00	0.0930 13	36.00	0.0927 42	35.00				
LD	0.0843 9/8/2000	400	0.1143 6	75.00	0.1133 11	72.50	0.1129 13	71.50	0.1125 42	70.50				

Sample	TSS mg/L
HR	2.00
LSF	14.75
OMC	35.00
LR	8.25
AC	14.00
OR	24.00
SR	35.00
LD	70.50

Figure 2A. Graphs of Total Suspended Solids in mg/L over time (August - September).

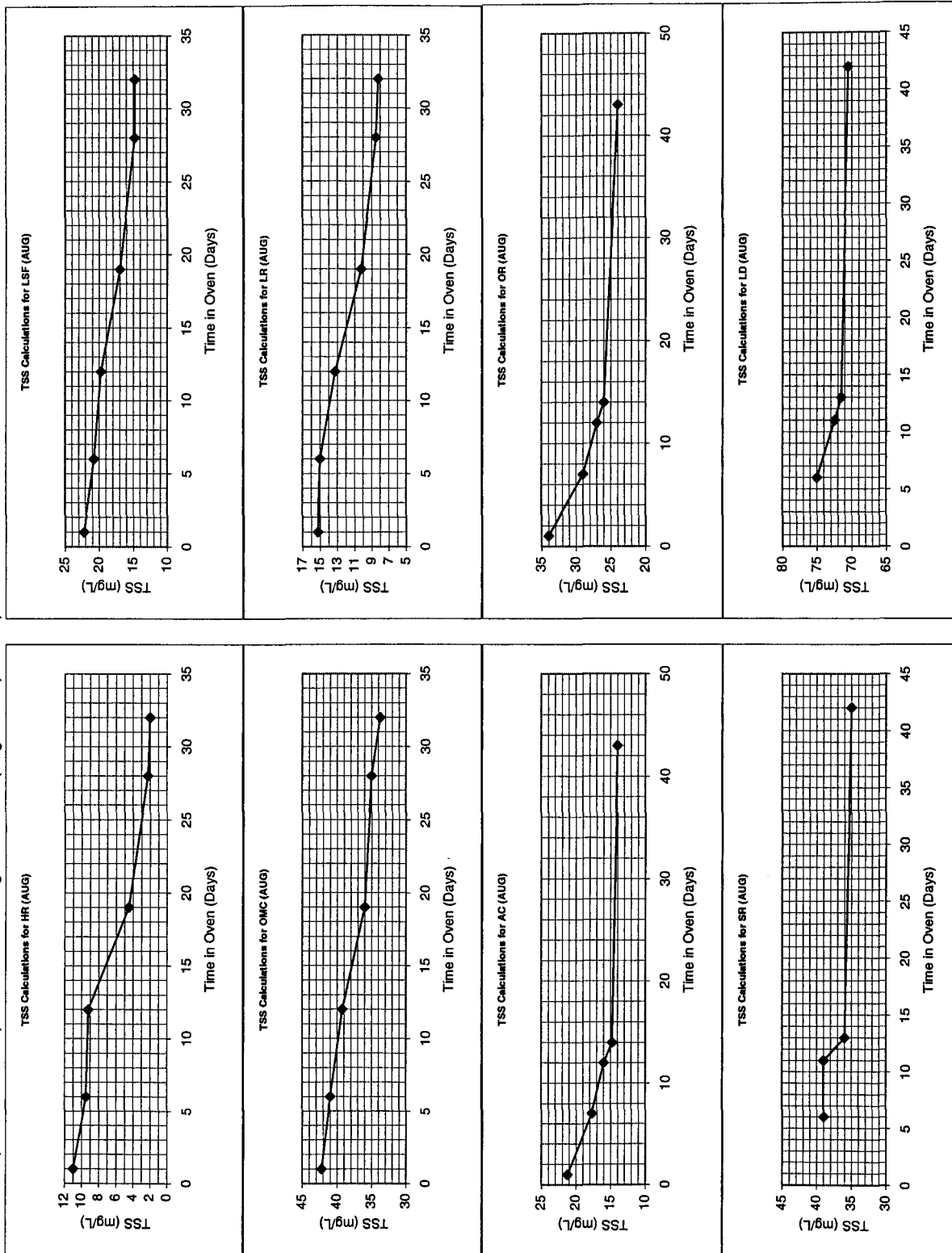
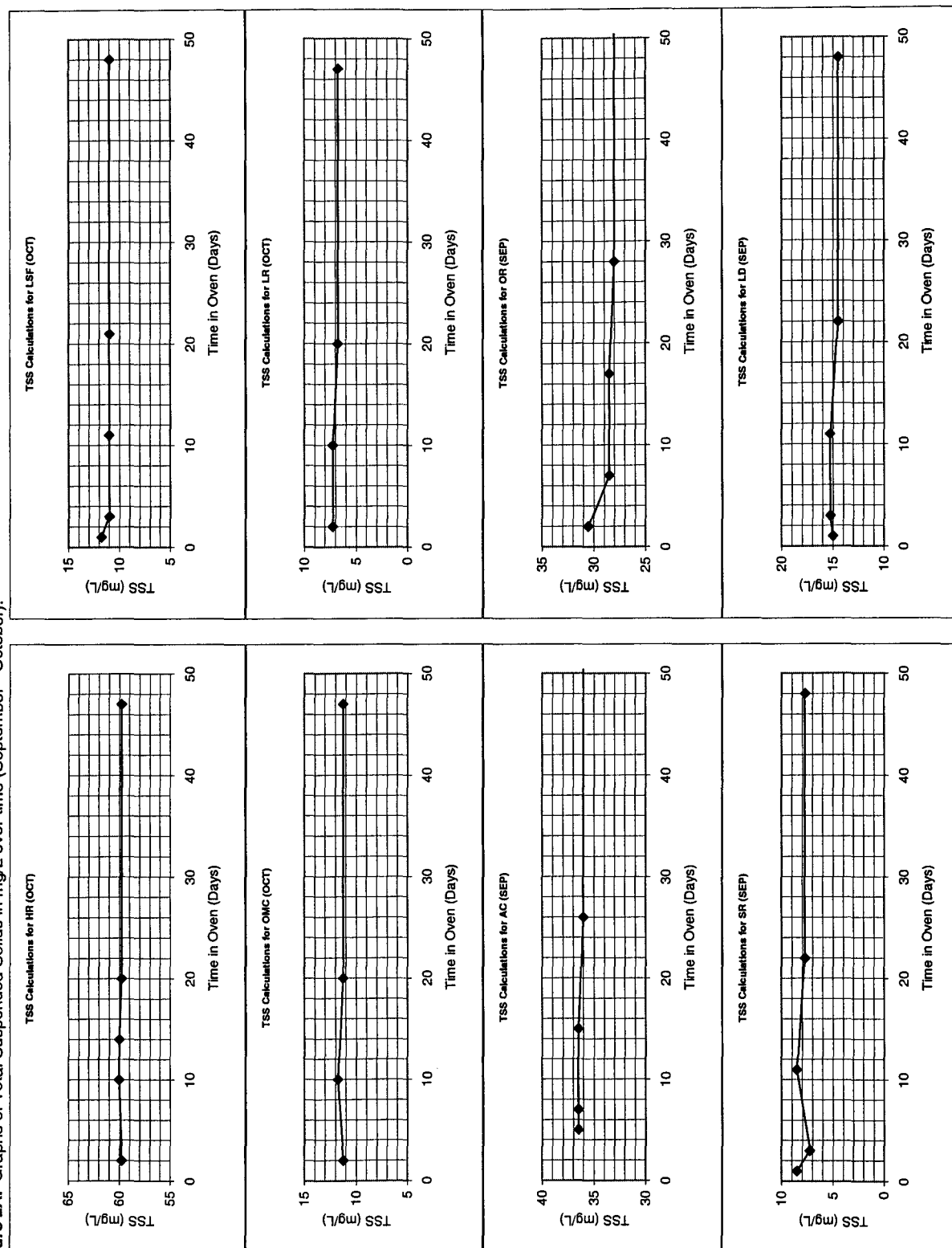


Table 4A. TSS data (September - October)

Sample	initial filter		volume of sample mL	filter+sample		filter+sample		filter+sample		filter+sample		filter+sample	
	weight after 3 days in oven g	3 days in oven g		days in oven g	mg/L	days in oven g	mg/L	days in oven g	mg/L	days in oven g	mg/L	days in oven g	mg/L
HR	0.0860 10/10/2000	0.1099 2	400	0.1100 10	59.75	0.1100 14	60.00	0.1099 20	59.75	0.1099 47	59.75	0.1099 47	59.75
LSF	0.0860 10/9/2000	0.0907 1	400	0.0904 3	11.75	0.0904 11	11.00	0.0904 21	11.00	0.0904 48	11.00	0.0904 48	11.00
OMC	0.0857 10/10/2000	0.0902 2	400	0.0904 10	11.25	0.0902 20	11.75	0.0902 47	11.25	0.0902 47	11.25	0.0902 47	11.25
LR	0.0859 10/10/2000	0.0888 2	400	0.0888 10	7.25	0.0886 20	7.25	0.0886 47	6.75	0.0886 47	6.75	0.0886 47	6.75
AC	0.0859 10/5/2000	0.1005 5	400	0.1005 7	36.50	0.1005 15	36.50	0.1003 26	36.00	0.1003 52	36.00	0.1003 52	36.00
OR	0.0855 10/3/2000	0.0977 2	400	0.0969 7	30.50	0.0969 17	28.50	0.0967 28	28.50	0.0967 54	28.00	0.0967 54	28.00
SR	0.0856 10/9/2000	0.0890 1	400	0.0885 3	8.50	0.0890 11	7.25	0.0887 22	8.50	0.0887 48	7.75	0.0887 48	7.75
LD	0.0858 10/9/2000	0.0918 1	400	0.0919 3	15.00	0.0919 11	15.25	0.0916 22	14.50	0.0916 48	14.50	0.0916 48	14.50

Sample	TSS mg/L
HR	59.75
LSF	11.00
OMC	11.25
LR	6.75
AC	36.00
OR	28.00
SR	7.75
LD	14.50

Figure 2A. Graphs of Total Suspended Solids in mg/L over time (September - October).



**Table 5A. Alkalinity data (AUG).**

Sample	pH	Milliliters of acid added	ALK (eq/L)	ALK (meq/L)	AVG (meq/L)	Stdev	%RSD	avg % diff
HR	4.5	0.738	0.0037	3.6900	3.7150	0.0354	0.9517	1.3459
	4.5	0.748	0.0037	3.7400				
LSF	4.5	0.900	0.0045	4.5000	4.4900	0.0141	0.3150	0.4454
	4.5	0.896	0.0045	4.4800				
OMC	4.5	0.306	0.0015	1.5300	1.5200	0.0141	0.9304	1.3158
	4.5	0.302	0.0015	1.5100				
LR	4.5	0.912	0.0046	4.5600	4.5450	0.0212	0.4667	0.6601
	4.5	0.906	0.0045	4.5300				
AC	4.5	0.710	0.0036	3.5500	3.5275	0.0318	0.9020	1.2757
	4.5	0.701	0.0035	3.5050				
OR	4.5	0.550	0.0028	2.7500	2.7400	0.0141	0.5161	0.7299
	4.5	0.546	0.0027	2.7300				
SR	4.5	0.888	0.0044	4.4400	4.4625	0.0318	0.7130	1.0084
	4.5	0.897	0.0045	4.4850				
LD	4.5	0.986	0.0049	4.9300	4.9450	0.0212	0.4290	0.6067
	4.5	0.992	0.0050	4.9600				

Standard  
Deviation

Relative  
Standard  
Deviation



**Table 6A.** Alkalinity data (SEP).

Sample	pH	Milliliters of acid added	ALK (eq/L)	ALK (meq/L)	AVG (meq/L)	Stdev	%RSD	avg % diff
HR	4.5	0.716	0.0036	3.5800	3.5600	0.0283	0.7945	1.1236
	4.5	0.708	0.0035	3.5400				
LSF	4.5	0.759	0.0038	3.7950	3.8075	0.0177	0.4643	0.6566
	4.5	0.764	0.0038	3.8200				
OMC	4.5	0.274	0.0014	1.3700	1.3625	0.0106	0.7785	1.1009
	4.5	0.271	0.0014	1.3550				
LR	4.5	0.922	0.0046	4.6100	4.6150	0.0071	0.1532	0.2167
	4.5	0.924	0.0046	4.6200				
AC	4.5	0.773	0.0039	3.8650	3.8650	0.0000	0.0000	0.0000
	4.5	0.773	0.0039	3.8650				
OR	4.5	0.465	0.0023	2.3250	2.3100	0.0212	0.9183	1.2987
	4.5	0.459	0.0023	2.2950				
SR	4.5	0.662	0.0033	3.3100	3.3275	0.0247	0.7438	1.0518
	4.5	0.669	0.0033	3.3450				
LD	4.5	0.951	0.0048	4.7550	4.6925	0.0884	1.8836	2.6638
	4.5	0.926	0.0046	4.6300				

Standard  
Deviation

Relative  
Standard  
Deviation

Table 7A. Average Molar concentrations (mmol/L) with respect to sampling locations and systems.

mmol/L	F	Cl	Br	SO <sub>4</sub>	Li	Na	K	Mg	Ca	Sr	Si	HCO <sub>3</sub> *	HCO <sub>3</sub> **
LR	0.0261	2.3963	0.0025	1.1113	0.0016	2.2206	0.1686	0.9755	1.9541	0.0080	0.0975	4.5800	3.6185
LSF	0.0228	2.8191	0.0000	0.7785	0.0006	2.6369	0.1982	0.9778	1.7542	0.0164	0.0886	4.1488	3.9337
HR	0.0157	1.9323	0.0000	0.8247	0.0010	2.2792	0.1222	0.8764	1.6639	0.0037	0.1196	3.6375	3.8994
OMC	0.0000	0.4326	0.0000	0.1137	0.0000	0.8484	0.0552	0.3512	0.6251	0.0000	0.1305	1.4413	2.1963
Sandstone	0.0215	2.3826	0.0008	0.9048	0.0011	2.3789	0.1630	0.9432	1.7907	0.0094	0.1090	4.1221	3.8139
AC	0.0252	1.1035	0.0005	1.4143	0.0019	0.9926	0.1442	1.2148	2.0273	0.0121	0.0789	3.6963	3.6878
OR	0.0224	0.7112	0.0000	0.4295	0.0005	0.7790	0.1000	0.7502	1.1252	0.0069	0.0310	2.5250	3.0512
SR	0.0426	1.4273	0.0015	1.4324	0.0017	2.0989	0.2400	0.9862	1.8708	0.0410	0.1462	3.8950	3.8002
LD	0.0343	0.8419	0.0010	0.6537	0.0010	0.6990	0.0985	1.3904	1.6625	0.0516	0.1087	4.8188	4.8230
Carbonate	0.0311	1.0210	0.0008	0.9825	0.0013	1.1424	0.1457	1.0854	1.6714	0.0279	0.0912	3.7338	3.8405

Note: Sandstone system average does not take into account OMC results

\* HCO<sub>3</sub> calculated using alkalinity titrations

\*\* HCO<sub>3</sub> calculated by ion charge balance

Analyte	Limit of Detection
Li	0.00042 mmol/L
Na	0.00236 mmol/L
K	0.00111 mmol/L
Mg	0.00625 mmol/L
Ca	0.00374 mmol/L
Sr	0.00138 mmol/L
Cl	0.00429 mmol/L
SO <sub>4</sub>	0.00060 mmol/L
F	0.00300 mmol/L
Br	0.00030 mmol/L

**Table 8A.** Carbonate geochemical modeling results using PHREEQE (Parkhurst et al, 1990).

PHASE	LOG IAP	LOG KT	LOG IAP/KT
<b>AC 29AUG2000</b>			
Calcite	-7.8202	-8.4619	0.6418
Aragonite	-7.8202	-8.3158	0.4956
Dolomite	-15.8391	-17.0126	1.1735
<b>AC 29SEP2000</b>			
Calcite	-7.9103	-8.4141	0.5038
Aragonite	-7.9103	-8.2598	0.3495
Dolomite	-16.0622	-16.7492	0.6870
<b>OR 29AUG2000</b>			
Calcite	-8.3882	-8.4693	0.0812
Dolomite	-16.9783	-17.0456	0.0673
<b>OR 29SEP2000</b>			
<i>All phases result in negative LOG IAP/KT values</i>			
<b>SR 29AUG2000</b>			
Calcite	-8.1428	-8.4625	0.3197
Aragonite	-8.1428	-8.3164	0.1736
Dolomite	-16.5387	-17.015	0.4763
Quartz	-3.8651	-4.0280	0.1629
<b>SR 29SEP2000</b>			
Calcite	-8.3313	-8.4235	0.0922
Quartz	-3.8082	-4.1581	0.3499
<b>LD 29AUG2000</b>			
Calcite	-7.5335	-8.4625	0.9289
Aragonite	-7.5335	-8.3164	0.7828
Dolomite	-15.1198	-17.0150	1.8951
Strontianite	-9.0268	-9.2688	0.2420
Quartz	-3.9905	-4.0280	0.0376
Talc	-60.5978	-62.6484	2.0506
<b>LD 29SEP2000</b>			
Calcite	-7.9642	-8.4219	0.4577
Aragonite	-7.9642	-8.2691	0.3049
Dolomite	-16.0237	-16.7999	0.7762
Quartz	-3.9478	-4.1645	0.2168

*All remaining phases in each model result in negative LOG IAP/KT values and were not considered*

**Table 9A.** Sandstone geochemical modeling results using PHREEQE (Parkhurst et al, 1990).

PHASE	LOG IAP	LOG KT	LOG IAP/KT
<b>LSF 23AUG2000</b>			
Calcite	-8.0136	-8.4563	0.4427
Aragonite	-8.0136	-8.3093	0.2957
Dolomite	-16.2939	-16.9864	0.6924
<b>LSF 04OCT2000</b>			
Calcite	-7.6468	-8.4408	0.7940
Aragonite	-7.6468	-8.2915	0.6447
Dolomite	-15.5297	-16.9091	1.3794
Quartz	-4.0305	-4.0952	0.0648
Talc	-62.9099	-63.1541	0.2441
<b>LR 23AUG2000</b>			
Calcite	-7.7967	-8.4614	0.6647
Aragonite	-7.7967	-8.3152	0.5185
Dolomite	-15.8520	-17.0102	1.1582
Quartz	-3.9968	-4.0311	0.0343
<b>LR 04OCT2000</b>			
Calcite	-7.9959	-8.4484	0.4525
Aragonite	-7.9959	-8.3002	0.3043
Dolomite	-16.3375	-16.9479	0.6104
Quartz	-4.0331	-4.0706	0.0375
<b>HR 23AUG2000</b>			
Calcite	-7.8266	-8.4609	0.6343
Aragonite	-7.8266	-8.3146	0.4880
Dolomite	-15.9091	-17.0078	1.0988
Quartz	-3.9051	-4.0326	0.1275
Talc	-61.1444	-62.6824	1.5380
<b>HR 04OCT2000</b>			
Calcite	-7.6164	-8.4451	0.8287
Aragonite	-7.6164	-8.2963	0.6800
Dolomite	-15.5247	-16.9310	1.4063
Quartz	-3.9551	-4.0813	0.1263
Talc	-62.2458	-63.0494	0.8036
<b>OMC 23AUG2000</b>			
Quartz	-3.9271	-4.0752	0.1481
<b>OMC 04OCT2000</b>			
Quartz	-3.8513	-4.1328	0.2815

*All remaining phases in each model result in negative LOG IAP/KT values and were not considered*